

formic acid,^{5,7,8,9} and by the dehydrohalogenation and hydrolysis of ethylidenecyclohexane nitrosochloride.¹⁰

¹ This investigation was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Government Synthetic Rubber Program.

² Darzens, *Compt. rend.*, **150**, 707 (1910).

³ Christ and Fuson, *J. Am. Chem. Soc.*, **59**, 895 (1937).

⁴ Nightingale, Milberger, and Tomisek, *J. Org. Chem.*, **13**, 358 (1948).

⁵ Hurd and Christ, *J. Am. Chem. Soc.*, **59**, 120 (1937).

⁶ Levina and Vinogradova, *J. Applied Chem. U.S.S.R.*, **9**, 1299 (1936) [*C.A.*, **31**, 2587 (1937)].

⁷ Rupe, Messner, and Kambli, *Helv. Chim. Acta*, **11**, 454 (1928).

⁸ Fischer and Löwenberg, *Ann.*, **475**, 203 (1929).

⁹ Chanley, *J. Am. Chem. Soc.*, **70**, 246 (1948).

¹⁰ Wallach, *Ann.*, **360**, 46 (1908).

ACRYLIC ACID

I. PYROLYSIS METHOD



Submitted by W. P. RATCHFORD.

Checked by ARTHUR C. COPE, WILLIAM R. ARMSTRONG, and JAMES J. RYAN.

1. Procedure

A 90-cm. length of 28-mm. (outside diameter) Pyrex tubing packed with pieces of Pyrex tubing (Note 1) is mounted vertically in an electric furnace (Note 2) capable of maintaining a temperature of 585-595°. A 250-ml. long-stemmed separatory funnel is connected to the upper end of the tubing with a stopper (Note 3), and the lower end is connected to a 500-ml. three-necked flask immersed in ice water. The flask, which serves as a receiver, is attached to a 50-cm. water-cooled reflux condenser, which in turn is connected by short lengths of rubber tubing to two traps in series which are immersed in a Dry Ice-trichloroethylene mixture. The exit tube of the second trap is vented to a hood. From 0.2 to 0.3 g. of hydroquinone is placed in the

receiver, together with a few pieces of Dry Ice which serve to displace air from the entire apparatus. The third neck of the receiver is stoppered.

The furnace is heated to 590° (Note 4), and after the air has been displaced 200 g. (216 ml., 2 moles) of ethyl acrylate (Note 5) is placed in the separatory funnel and admitted to the reaction tube at a rate of about 90 drops a minute (Note 3), so that the addition requires about 2 hours. At the end of the addition the contents of the receiver and the small amount of liquid in the traps are combined. The total weight of crude acrylic acid containing some ethyl acrylate is 126–136 g.

The crude product is placed in a 250-ml. flask containing a capillary inlet tube through which carbon dioxide is admitted. Ten grams of hydroquinone and 15 g. of diphenyl ether are added, and the flask is attached to a suitable fractionating column (Note 6). The product is fractionated carefully (Note 7) at 135 mm. pressure. The pressure is lowered gradually when most of the ethyl acrylate has distilled, and at about 70°/90 mm. the receiver is changed. The first fraction (mostly ethyl acrylate) amounts to 9–10 g. The pressure is lowered further to 50 mm., and the acrylic acid is distilled fairly rapidly, without reflux, at 69–71°/50 mm. The acrylic acid fraction weighs 108–116 g. and is 95–97% pure according to acidimetric titration. The yield is 68–75% based upon 100% acrylic acid content (Notes 8 and 9).

If the acrylic acid is not to be used at once, it is stabilized by the addition of hydroquinone and is stored in a refrigerator.

2. Notes

1. The middle third of the Pyrex tube should be packed with 20-mm. lengths of fire-polished 7-mm. Pyrex tubing. The lower end of the tube is drawn out to a size that permits attachment to the receiver with a rubber stopper.

2. A type FD303 combustion furnace (made and sold by the Hoskins Manufacturing Company, Detroit, Michigan) or any similar furnace is satisfactory.

3. A groove filed in the stopcock of the separatory funnel aids in controlling the rate of addition. If available, a small constant-

feed pump may be used to introduce the ester into the pyrolysis tube. The rate of addition of the ester is not critical, but at high rates cracking is incomplete and at low rates the yield is reduced. A slow stream of nitrogen (100 bubbles per minute) flowing through the tube reduces refluxing and makes the feed rate easier to observe. The nitrogen may be introduced through a tube in the stopper holding the separatory funnel or through a side arm sealed near the upper end of the pyrolysis tube.

4. The temperature is measured by a movable Chromel-Alumel thermocouple located in the furnace by the side of the tube and connected to a potentiometer or millivoltmeter. The thermocouple junction is adjusted so that during the run it is at the hottest point in the furnace. For the Hoskins Company furnace this point is about 9 in. from the top of the furnace. The temperature is controlled manually to $590 \pm 5^\circ$ by means of an autotransformer (Variac) rated at 5 amperes, 110 volts.

5. Commercial ethyl acrylate, containing hydroquinone inhibitor, may be used directly if it is of good quality.

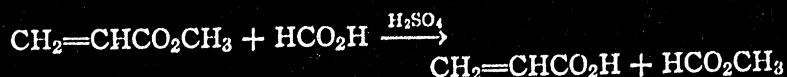
6. The submitter used an insulated column with a 38 by 1.1 cm. section packed with $\frac{1}{8}$ -in. copper helices made of No. 26 B & S gauge copper wire. He states that a column packed with glass helices is unsatisfactory. The checkers used a 100 by 1.7 cm. Vigreux column. Either type of column should be equipped with a total condensation, partial take-off head.

7. Ethyl acrylate and acrylic acid polymerize easily, and overheating must be avoided in the distillation. The flask is heated in an oil bath which is not permitted to rise above 115° . The diphenyl ether which is added serves to expel the acrylic acid at the end of the distillation.

8. The submitter states that the product may be purified by freezing and decanting the supernatant liquid several times. The acrylic acid may be obtained in 97% purity by this method, but it has a faint yellow color. The yield is 50 to 60%.

9. The submitter states that methacrylic acid may be prepared in a similar manner by pyrolyzing ethyl methacrylate. Under the same conditions of temperature and feed rate, the conversion is slightly higher and the yield is about the same.

II. ACIDOLYSIS METHOD



Submitted by C. E. REIBERG.

Checked by ARTHUR C. COPE and ELBERT C. HERRICK.

1. Procedure

One hundred and eighty-four grams (151 ml., 4 moles) of formic acid (Note 1), 1032 g. (1060 ml., 12 moles) of methyl acrylate (Note 2), 30 g. of hydroquinone, and 2 ml. of sulfuric acid are mixed in a 2-l. two-necked round-bottomed flask fitted with a capillary inlet tube. The flask is attached to a 100 by 1.7 cm. Vigreux column (Note 3) and is heated in an oil bath at 85–95°. The mixture is heated under total reflux until the temperature of the vapor at the still head falls to 32° (after 1–3 hours). Methyl formate then is distilled slowly at 32–35° as long as it is formed (8–10 hours). A reflux ratio of about 5 to 1 is maintained during the first part of the distillation, which is decreased to total take-off at the end. When no more methyl formate is produced, the excess methyl acrylate is distilled at 32–35°/140 mm. with the bath temperature at 60–65°. During the distillation, a slow stream of carbon dioxide is admitted through the capillary inlet. When all the methyl acrylate has been removed, the acrylic acid is distilled at 53–56°/25 mm. Upon redistillation through the same column (Note 4) acrylic acid of 97% purity (by acidimetric titration) is obtained in a yield of 220–230 g. (74–78% based upon 100% acrylic acid content), b.p. 54–56°/25 mm.

2. Notes

1. Acetic acid may be used, but it reacts much less rapidly and less completely, and fractionation of the reaction mixture is more difficult. Pure formic acid (98–100%) is preferred.

2. Commercial methyl acrylate may be used without purification if it is of good quality.

3. Either a Vigreux column or a column containing an open

spiral of copper or Nichrome wire is satisfactory. The column should be jacketed and fitted with a total condensation, variable take-off head.

4. Hydroquinone or another polymerization inhibitor should be added before distillation of acrylic acid or its esters.

3. Methods of Preparation

Acrylic acid free of water has been prepared by treating lead acrylate with hydrogen sulfide;^{1,2} by heating α,β -dibromopropionic acid with copper;³ by dry distillation of a mixture of equivalent amounts of sodium acrylate and β -chloropropionic acid,⁴ and by the two methods described in these preparations.⁵

¹ Caspary and Tollens, *Ann.*, **167**, 252 (1873).

² Wohlk, *J. prakt. Chem.*, (2) **61**, 212 (1900).

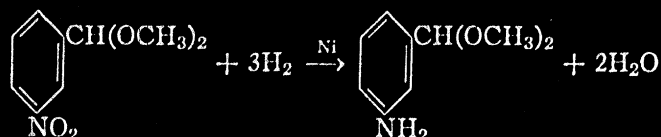
³ Biilmann, *J. prakt. Chem.*, (2) **61**, 491 (1900).

⁴ Riiber and Schetelig, *Z. physik. Chem.*, **48**, 348 (1904).

⁵ Ratchford, Rehberg, and Fisher, *J. Am. Chem. Soc.*, **66**, 1864 (1944).

m-AMINO BENZALDEHYDE DIMETHYLACETAL

(Benzaldehyde, *m*-amino-, dimethylacetal)



Submitted by ROLAND N. ICKE, C. E. REDEMANN, BURNETT B. WISEGARVER, and GORDON A. ALLES.

Checked by H. R. SNYDER and FRANK X. WERBER.

1. Procedure

In a 1-l. steel bomb¹ are placed 295 g. (1.5 moles) of *m*-nitrobenzaldehyde dimethylacetal (p. 72), 250 ml. of technical anhydrous methanol, and 1 tablespoon of Raney nickel catalyst.² Hydrogen is introduced until the pressure is about 1000 lb. (Note 1). The bomb is heated to about 40°, at which point the heating is discontinued and the shaker is started. The hy-

drogenation soon becomes rapid as the temperature rises to about 70° (Note 2). The bomb is refilled with hydrogen as many times as necessary (Note 3). The theoretical amount of hydrogen (4.5 moles) is absorbed in about 1.5 hours.

The bomb is cooled, the remaining hydrogen is discharged, and the bomb is opened. The solution is transferred to a beaker, and the bomb is rinsed with a little methanol which is added to the solution. The catalyst is removed by filtration (*Caution! The catalyst may be pyrophoric*), and most of the filtrate is transferred to a 500-ml. Claisen flask set on a steam bath for distillation of the methanol; the remainder of the filtrate is introduced into the Claisen flask when the volume of the first portion has been reduced sufficiently by distillation. After all the methanol has been removed the aminoacetal is distilled under diminished pressure. The yield of *m*-aminobenzaldehyde dimethylacetal, a light-yellow liquid boiling at 123–124°/4 mm. or 110–112°/1.5 mm., is 168–196 g. (67–78%).

2. Notes

1. The hydrogenation is similar to one described earlier.¹ As the bomb does not contain enough hydrogen to complete the reduction, more hydrogen should be admitted whenever the pressure drops below 300 lb.

2. Because of the high heat capacity of the bomb the internal temperature continues to rise (to about 70°) after the heater is turned off. As the exothermic hydrogenation begins the temperature rises to about 80°. The temperature should be kept below 85° to prevent hydrogenolysis of the acetal.

3. If the hydrogenation is started at a pressure of about 1500 lb. in a 2.5-l. bomb it will not be necessary to introduce more hydrogen. However, it may be necessary to stop the shaker occasionally to prevent a temperature rise beyond 85°.

3. Methods of Preparation

This acetal has not been described previously. The corresponding diethylacetal has been prepared by the reduction of